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DILUTE ACID HYDROLYSIS OF HIGH SOLIDS WOOD SLURRIES IN A TWO-STAGE CONTINUOUS FLOW PROCESS

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ABSTRACT

Research in SERI's Biotechnology Branch has addressed the technical feasibility of pumping high-solids wood slurries (>18%) in a continuous two-stage acid hydrolysis process. The research was intended to resolve a primary uncertainty in the potential of the technology to produce fermentable sugars for fuel-grade ethanol. The results of this research are described in the attached report.

The approach of the experiments was to prehydrolyze the wood at mild conditions prior to the hydrolysis reactor, thereby degrading the hemicellulose. The resultant prehydrolyzate slurry resists the plugging, dewatering and bridging typical of water-wood mixtures and can be pumped more easily at relatively high concentrations (>18%).

The SERI experiments encountered several major equipment problems that delayed progress. Problems with the automatic wood feeder and the airlock hopper were resolved, but problems with the Moyno progressing cavity pump remain. The pump problems prevented sufficient operation to demonstrate pumpability of the high solids slurries. However, we believe that some limited additional testing with a new Moyno pump would provide sufficient data to successfully demonstrate the process. Currently, work is being continued with funding by a private company that is interested in commercializing the process for the production of specialty chemicals.

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INTRODUCTION

The hydrolysis of cellulose has been studied extensively by a number of researchers for the production of fermentable sugars. Work on dilute acid hydrolysis was widespread during World War II in the U. S. and elsewhere. The process produces sugars and their degradation products, depending on acid concentration, reaction temperature and reaction time. The reaction theory was reviewed in a previous paper *(Brennan et. al. 1986)*.

Most of the early work was based on percolation reactors which generally have long residence times and produce a dilute sugar stream. Several researchers have investigated continuous slurry flow systems which can operate at higher temperatures and shorter reaction times, producing higher yields (Katzen and Othmer 1942, Grethlein and Converse 1982, Kwarteng 1983). Most of these projects, however, used dilute wood slurries, because of the difficulties inherent in processing high solids concentrations. This limitation results in a dilute sugar stream that is uneconomic to recover. Two projects did address high solids processing *(Church and Woolridge 1981, Rugg 1982)*, but neither produced an economic process because of expensive equipment or operating problems.

The current SERI experiment is based on work performed over the last several years at Dartmouth College and Badger Engineers, Inc., using plug flow reactor technology. The plug flow reactor has several potential advantages over other processes. First, the reactor can achieve short residence times at high temperatures, resulting in higher product yields than possible with other dilute acid systems. In addition, because of the short residence time, the reactor can be smaller and less expensive than percolation reactors or extruders. Finally, the conditions required for high glucose yield produce furfural as a degradation product of xylose--furfural is a valuable byproduct that may provide a significant cash flow for a near-term wood-to-ethanol plant.

Under subcontract to SERI, researchers at Dartmouth and Badger have investigated several aspects of dilute acid hydrolysis using a plug flow reactor. Over several years at Dartmouth, Grethlein and Converse *(1982)* and Kwarteng *(1983)* have developed kinetic parameters for glucose, xylose and furfural yields in laboratory-scale experiments. Glucose yields from hardwood flour ranged as high as 55% in Kwarteng's work, showing that high yields were obtainable on a small-scale. However, they encountered several operational problems such as tar buildup and rapid plugging that were difficult to solve on a small scale.

Badger Engineers, Inc. conducted an engineering analysis of dilute acid hydrolysis *(1982)*. Using plug flow reactor technology, they designed a commercial-scale ethanol production plant with a capacity of 94.6 x 10^6 L/yr

(25.0×10^6 gal/yr) and determined capital and operating costs. The study concluded that ethanol could be produced for \$0.32/L to \$0.87/L (\$1.23-3.31/gal), depending on economic assumptions, byproduct credits, reactor yields and solids concentration in the reactor. Badger identified high solids processing (at least 18% by weight) and operating experience at an engineering scale as critical to the eventual success of the technology.

The experiment at SERI was designed to address these issues by testing a concept suggested by Badger for hydrolyzing concentrated wood slurries (>18%) in a two-stage process. In this process, wood flour is prehydrolyzed in a first-stage reactor, degrading the hemicellulose and producing a slurry resistant to plugging, dewatering and bridging. The slurry is then pumped to the hydrolysis reactor where the reaction is completed. In this manner, more concentrated product streams should be produced.

The experiment was carried out in two phases. The first phase involved a single stage hydrolysis process with low solids slurries (10%) to replicate Dartmouth's data at a larger scale and to provide a baseline for later work. This phase was completed in May 1986 and documented in a SERI report *(Brennan and Schell 1986)*. During the second phase, reported on in this paper, the equipment was modified for the two-stage process, and experiments were conducted to determine the feasibility of high-solids processing.

SYSTEM DESCRIPTION

The plug flow acid hydrolysis experiment is designed to determine the feasibility of hydrolyzing high solids wood slurries using dilute sulfuric acid on an engineering scale. A simplified process flow schematic is shown in Figure 1.

The hydrolysis reaction takes place in two steps. In the first, wood flour, hot water and sulfuric acid are fed into the 190-L (50-gal) prehydrolysis reactor (PHRX) continuously to achieve the desired solids and acid concentrations. The PHRX operates at temperatures of 140-170°C and residence times of 5-10 min. The resultant slurry is then pressurized by a progressing cavity pump to 4.6 MPa (650 psig) and flows to the plug flow hydrolysis reactor (HRX). In this reactor, the hydrolysis reaction is completed at temperatures of 240-260°C and residence times of 4-10 sec. The products of the reaction are flashed to 415 kPa (75 psig), and the vapor and liquid phases are separated, cooled, collected and analyzed.

The system is divided into four subsystems: the prehydrolysis equipment, the hydrolysis equipment, the flash vapor recovery equipment and the hydrolyzate recovery equipment. This section describes each subsystem in more detail.

Prehydrolysis Subsystem

The prehydrolysis section consists of a 190-L (50-gal) reactor and the associated equipment for feeding wood flour, water, steam and acid at the

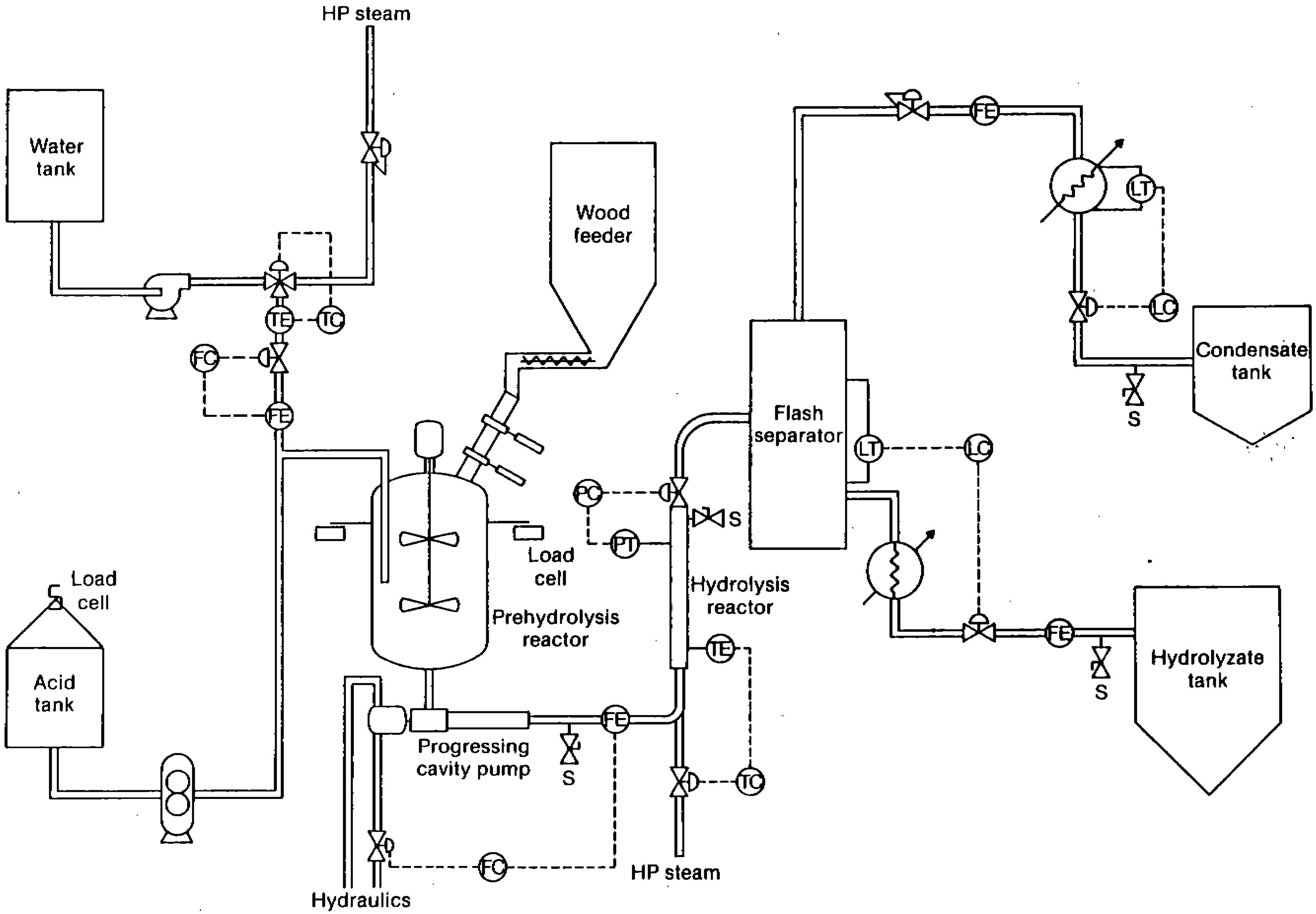

Figure 1. Schematic of the Plug Flow Acid Hydrolysis Experiment

rates required to achieve desired solids and acid concentrations, reactor temperature and residence time.

The heart of the prehydrolysis subsystem is the continuous stirred tank reactor, designed by and fabricated for SERI from 316L stainless steel. The reactor is jacketed and has numerous penetrations for material addition and instrumentation. A hydraulic turbine agitator is installed in the head of the reactor to ensure thorough mixing of the wood slurry. The reactor is mounted on three BLH (5 kN) load cells which are used to determine the weight of the reactor contents.

Water is pumped from a tank to the prehydrolysis reactor (PHRX) by a Gould 3333 14-stage centrifugal pump. The water is heated to 140-160°C by a HydroHeater M101 mixing valve which adds 1.5 MPa (200 psig) steam to achieve the desired temperature. The flow rate of the hot water is controlled by a loop consisting of a MicroMotion D40 mass flow meter, a Foxboro 760 self-tuning controller, and a Research Control Valve. The water enters the reactor through a dip-tube which projects to the bottom of the reactor and is penetrated by several sets of holes.

Concentrated sulfuric acid (93%) is metered into the reactor by a Durcometer B1060 double diaphragm metering pump. The 40-L (10-gal) acid storage tank is suspended from a BLH load cell to monitor acid flow rate.

Wood flour is added to the PHRX by a VibraScrew loss-in-weight feeder with a 0.6 m^3 (20 ft^3) hopper. At the bottom of the hopper, two rotating blades supply wood at a constant bulk density to the main feed screw. The speed of the screw is controlled automatically to feed the appropriate mass flow rate as measured by a load cell. Since the wood flour in the hopper tends to form bridges, ratholes and chimneys, a bridge-breaking device was installed to ensure continuous flow to the screws. The device is based on an invention developed and patented at SERI by Diebold and Scahill *(1986)*.

The wood flows from the feeder, through a plexiglass boot, and into an airlock mounted on the top of the prehydrolysis reactor. The airlock, designed and fabricated at SERI, allows wood to be added to the reactor without bleeding down the reactor pressure or allowing steam to escape into the wood supply. The airlock consists of two 6-inch pneumatically actuated knife gate valves, a 6-inch pipe hopper in between, and the valves and controls required to cycle the knife gate valves and pressurize the intermediate chamber. During a typical cycle, the top valve opens, wood drops into the chamber and the top valve closes. The chamber is then pressurized with inert gas to a pressure slightly higher than reactor pressure. The bottom valve opens and the wood drops into the reactor. Smooth flow of the wood is ensured by the injection of inert gas at several points above both knife gate valves. The airlock system is controlled by the computer which runs the data acquisition program, described in a later section. The design of the airlock is described in more detail by Schell *(1987)*.

The flow rates of the wood and hot water inlet streams are controlled by a Foxboro 760 controller to provide the desired solids concentration and prehydrolysis residence time. The controller actually seeks to regulate the weight of the reactor contents, sensed by the reactor load cells, thereby controlling residence time. The ratio output feature of the level controller supplies remote set points to both the wood feed rate controller and the water flow rate controller to regulate the input streams in the correct proportion.

The PHRX pressure is controlled by a Fisher 98-H pressure relief valve, designed to bleed off the inerts introduced through the airlock and maintain a constant reactor pressure. The bleed stream, which contains some steam, is cooled, condensed and collected for later analysis.

Hydrolysis Subsystem

The hydrolysis subsystem is designed to bring the prehydrolyzed slurry to the desired hydrolysis conditions and provide the correct residence time for the reaction to be completed. The prehydrolysis reactor is directly coupled to a hydraulically driven Moyno 9P4 progressing cavity pump with a viton stator and an undersized stainless steel rotor. The viton stator swells due to the temperature of the slurry; this swelling provides the clearances required to achieve the output pressure of 4.6 MPa (650 psig).

Just downstream of the pump, the flow rate of the slurry is measured by a Polysonics UF84 ultrasonic flowmeter. This flowrate is controlled by a Fisher analog controller which regulates Moyno pump speed by varying the hydraulic flow rate to the motor through a Worcester electrically actuated ball-type control valve. The prehydrolyzed slurry flows from the pump to the hydrolysis reactor. The reactor is 3.8 cm (1.5 in.) in diameter and 1.2 m (4 ft) long, and is fabricated from Schedule 80 Hastelloy C-276 pipe and fittings. The reactor is mounted vertically to prevent buildup of pockets of uncondensed steam. The slurry is introduced to the reactor through a long-radius elbow at the head of the reactor to induce swirling. High pressure steam (5.6 MPa, 800 psig) is injected at the elbow through a full cone Hastelloy spray nozzle, consisting of twenty 0.13-cm (0.05-in.) holes drilled at angles up to 45° to the flow. The flow of steam is regulated by a Fisher analog controller to control temperature within the reactor as measured by a thermocouple in the flow path downstream of the reactor entrance.

At the reactor discharge, the products flow through a globe-type pressure letdown valve, made by Masonelian, the purpose of which is two-fold. First, the valve serves to control the reactor pressure, sensed by a Foxboro 821GH pressure transmitter near the end of the reactor. Second, the rapid pressure and temperature drop through the valve quench the reaction, preventing degradation of the products.

The products flow through the pressure letdown valve into the flash separator, a 0.3-m (1.0-ft) diameter vessel designed by and fabricated for SERI from schedule 40 stainless steel 316L pipe and fittings. The separator is 1.4 m (4.5 ft) tall and is equipped with a 15-cm (6-in.) thick Fleximesh mist eliminator pad near the top. The liquid level in this tank is maintained by a control loop consisting of a diaphragm type Foxboro 823DP differential pressure transmitter, a Fisher analog controller, and a flow control valve, described below in the Hydrolyzate Recovery Section.

Flash Vapor Recovery Subsystem

The vapor stream exiting the flash separator consists of steam, with small amounts of furfural, acetic acid, and some noncondensables. The flow rate of the vapor stream is controlled by a Taylor back-pressure regulator which controls separator pressure to about 415 kPa (75 psig). The stream flows through a Micromotion D100 mass flowmeter which determines mass flow directly based on the Coriolis effect.

The vapor stream then flows to a condenser, a conventional shell and tube heat exchanger supplied by American Standard (Model SSCF-8036). The level of condensate is regulated by a level control loop based on a Foxboro 823DP differential pressure transmitter. Condenser pressure is regulated by a Nupro pressure relief valve which bleeds off noncondensables. The condensate is stored in a 1100-L (300-gal) cross-linked polyethylene tank.

Hydrolyzate Recovery Subsystem

The liquid phase leaving the flash separator contains sugars, other hydrolysis products, sulfuric acid and some unreacted solids. The flow of the hydrolyzate is regulated by the level control loop on the separator, as described earlier, to ensure that the hydrolyzate leg runs liquid full. A Red Valve 0.5-in. air-operated pinch valve is used to minimize plugging. The hydrolyzate is cooled in an American Standard SSCF-8078 four-pass horizontal shell and tube heat exchanger, and then flows through an Exac EX120 mass flow meter. The stream is stored in a 3800-L (1000-gal) polyethylene tank.

EXPERIMENTAL PROCEDURES

This section describes the operation of the experiment and data acquisition.

Feedstock

For the SERI experiments, Wilner 060 hardwood flour was selected for the feedstock for consistency with previous research (3,4,8). This flour is -60 mesh in size and is comprised primarily of poplar. Towards the end of the second phase of testing, larger particle sizes were tested using Wilner CB4 hardwood. This is the same mixture of hardwoods as the flour, but the particles range from 8 to 20 mesh in size.

Equipment Startup

Each experiment is begun by bringing the equipment up to reaction conditions on water, acid and steam. Water is heated to the desired temperature and injected into the prehydrolysis reactor. Acid is pumped separately into the reactor at the desired flow rate. Steam flows to the reactor jacket. Slowly, the reactor temperature, pressure and level come to the desired conditions. The Moyno pump is started up at a speed selected to provide the approximate desired flow rate. As the viton stator in the pump swells from the hot water, the hydrolysis reactor pressure control valve can be closed to achieve the desired pressure. At this point, high pressure steam is introduced into the hydrolysis reactor to bring its temperature to the desired level. The remainder of the product separation and collection equipment is brought on line as the temperature rises. Finally, when all the equipment and control loops are operating smoothly at the desired conditions, the wood feeder is turned on to begin feeding wood to the prehydrolysis reactor.

Experimental Design

Product yields from the two-stage plug flow experiment were predicted using Saeman's model (1945) with kinetic parameters developed by Kwarteng at Dartmouth (1983) with hardwood flour. Using these parameters, graphs of the product yields were prepared and are shown in Figures 2 and 3. Figure 2 shows the extent of the reaction at typical prehydrolysis conditions. As can be seen, there is little cellulose hydrolysis at these conditions. In Figure 3, hydrolysis conditions for maximum glucose yield are shown. From this graph it is evident that glucose yields above 50% should be attainable with residence times of about 5 to 8 sec at 245°C. At these conditions, the remaining hemicellulose hydrolyzes rapidly to xylose, which then degrades to furfural.

These kinetic relationships were used to establish operating conditions for the second phase experiments. The prehydrolysis reactor was maintained at 165°C and 100 psig with 1% acid concentration. The residence time for this reaction was approximately 5 minutes. Hydrolysis conditions were selected to provide maximum glucose yields.

Data from pressure, temperature, mass flow, level and weight instruments are recorded continuously using a microcomputer-based data acquisition system. An IBM PC controls the Keithley/DAS 500 data acquisition using a LabTech software package. The software controls data sample rate, performs units conversions, and stores data for later analysis. In these experiments data were recorded every 2 sec.

EXPERIMENTAL RESULTS

Equipment for the prehydrolysis unit was installed in the fall of 1986 and check-out was completed on schedule in October. During start-up, several problems were encountered with key pieces of equipment which took several months to resolve. Consequently, continuous operation with 18% solids was never achieved. However, as a result of the significant amount of operating experience gained during that period, we have determined the cause of the problems and believe they could be solved with some equipment modification. The problems with the wood feeder, the slurry pump, and the airlock are described below.

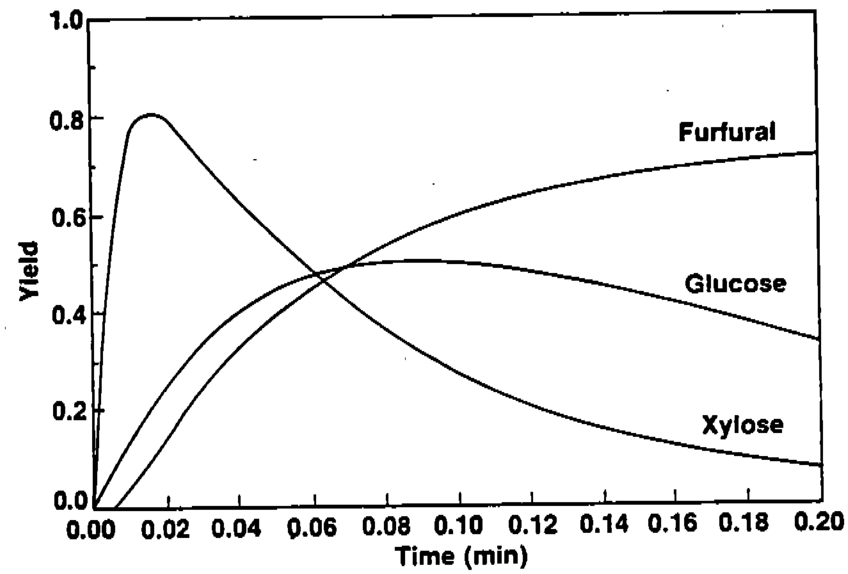

Figure 3. Hardwood Flour Hydrolysis Products at 255° C, 1% H_2SO_4

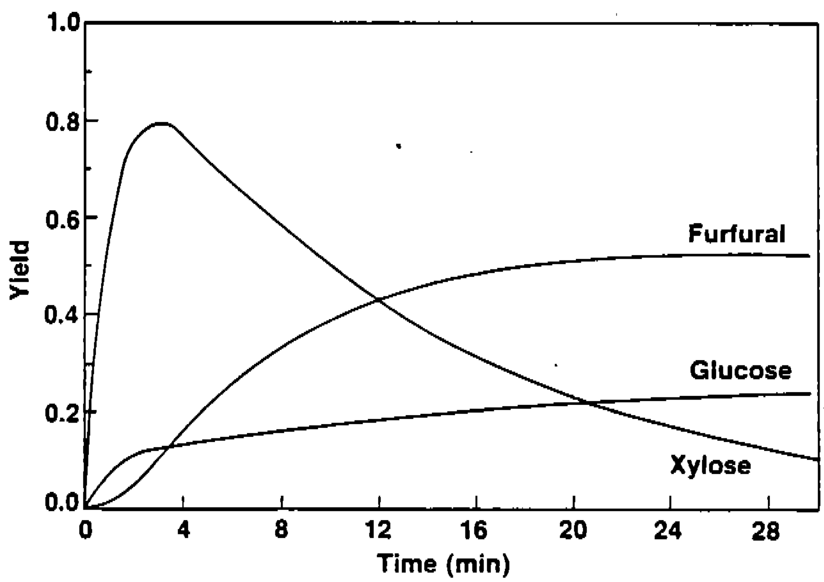

Figure 2. Hardwood Flour Prehydrolysis Products at 167° C, 1% H_2SO_4

Problems were first encountered with the Vibrascrew automatic wood feeder. The feeder is designed to feed wood to the airlock at the desired mass flow rate. Delivery of the feeder was two months later than the promised delivery date, and a number of problems became apparent at start-up. As delivered, the control panel for the wood feeder was missing the controller microprocessor, and much of the wiring was incorrect or incomplete. The panel was sent back to the manufacturer for rewiring, but after reinstallation, two visits from a factory representative were still necessary before operation could be established. In all, three months elapsed before these problems were resolved, significantly delaying further start-up activities.

In addition to the wood feeder, the Moyno progressing cavity pump proved problematic. Based on recommendations from the vendor, the pump was ordered with a viton stator and a standard-sized stainless steel rotor. This combination was designed to achieve adequate output pressure as the viton swelled from the elevated temperature of the prehydrolyzate. Like the wood feeder, the pump was delivered two months behind schedule. During start-up runs on water and steam in December, the pump seized and failed as the prehydrolysis temperature approached 100°C, significantly below the desired operating temperature. Discussions with the manufacturer revealed that the pump had been shipped with an oversized rotor instead of the standard, thereby reducing the clearances between the rotor and stator.

Several months of delays ensued as different rotors were tried in the pump. In addition, the viton stator was damaged due to the initial failure, and replacement by the vendor required a several week manufacturing process. We eventually settled on an undersized rotor, which provided adequate flow and output pressure at prehydrolysis operating conditions. This combination was finally received and installed at the end of April.

At the beginning of May, initial experiments with wood flour were begun. Operation was relatively smooth with the exception of the performance of the airlock. The vent line from the intermediate pressurized chamber tended to plug due to the poor flow characteristics of the wood flour and some steam leakage past the seat of the lower gate valve. Several modifications to the airlock improved the performance, but not sufficiently to achieve steady operation at the desired reaction conditions. Therefore a different feedstock was used which had larger particle sizes and much better flow characteristics. In addition, the pressurization connection on the airlock was moved to one large port instead of the multiple nozzles along the interior chamber walls to minimize fluidization of the wood. Following these changes, the airlock operated successfully during the final trials.

During the last few runs, the performance of the Moyno pump deteriorated, eventually making it impossible to achieve the required output flow and pressure. The viton was apparently sustaining wear because of the close fit between the rotor and stator at the prehydrolysis operating conditions. A standard-sized rotor was installed in the pump, and a final attempt at operation was made. However, the pump seized as prehydrolysis operating conditions were approached, and operation could not be maintained.

CURRENT WORK

SERI has received funding by a private firm through Badger Engineers, Inc for some additional work to support commercialization of the high-solids, dilute-acid plug flow process for the production of specialty chemicals. In cooperation with Bagder, SERI is now operating the plug flow experiment at low solids levels (less than 10%) to investigate solids deposition in the hydrolysis reactor, long term operational stability of the system, and chemical yields (primarily levulinic acid). The work has been divided into two phases: Initially, we are measuring chemical yields and solving the solids deposition problem. Typically, operating the plug flow reactor has been limited to less than four hours due to plugging of the hydrolysis reactor. Therefore, several techniques for reducing the solids buildup are being tried. When the plugging problems have been eliminated or significantly reduced, the second phase of the work will examine operational stability of the system during extended runs (24 hours or more) for high solid levels (approximately 18%).

CONCLUSIONS AND RECOMMENDATIONS

It was anticipated at the outset of the experiment that the performance of two key elements of the prehydrolysis unit--the airlock hopper and the slurry pump--was uncertain and that each would be critical to the success of the experiment. Extra attention was given to both of these items in the design phase, since our application deviated significantly from current industrial applications. After surveying the literature and talking with vendors, we decided to design and build our own airlock hopper. As discussed above, the airlock did not initially provide continuous feeding of wood flour but performed well with larger wood particles after some modification. We believe this design would provide consistent performance with extended operation.

A similar review process for the slurry pump identified two candidates: the Moyno progressing cavity pump and the Worthington twin screw pump. Both appeared adequate for the service, but the Worthington pump had a price and delivery that were incompatible with the task budget and schedule ($45,000 and twenty weeks for the Worthington vs. $9,000 and eight weeks for the Moyno). In addition, since Worthington would not perform any tests on our slurry without a purchase commitment, we couldn't be sure the Worthington would provide the required service. On the other hand, Moyno engineers performed tests with our prehydrolyzate samples and concluded that their pump would do the job. Therefore, the Moyno pump was selected. Unfortunately, Moyno's recommendation was based on fluid property tests and not full-scale pump tests. In addition, even a full-scale pump test probably would not have predicted the rapid stator wear which we saw in our experiments.

Aside from equipment problems typical of a hardware-intensive project such as this experiment, the slurry pump performance was the only significant problem which prevented the demonstration of high solids pumping. This was caused by the design and rapid wear of the pump itself and not by the pumpability of the prehydrolysis slurry, which we never made on a continuous basis. We believe some additional testing with a new Moyno stator could provide sufficient data to demonstrate the pumpability of a prehydrolyzed slurry. While this would not result in a configuration that could support continuous operation in an industrial setting, it should provide the basis for further development of an adequate pumping alternative. Finding a pump that could provide industrial service would probably involve significant time and resources and could perhaps best be accomplished as a development task with some industrial interest or support. We remain confident that the pumping problem can be resolved and that this technology shows significant potential as a method of producing fermentable sugars from wood for conversion to a liquid fuel.

Perhaps the most significant development of this work has been the interest of industry in commercializing this process, as exemplified by the follow on work for Badger Engineers, Inc. Several issues which we did not have the time to resolve can now be addressed, namely, eliminating solids buildup in the hydrolysis reactor, long term operational stability, and processing of high solid slurries.

ACKNOWLEDGEMENTS

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